

# On the Effect of Asphericity of the Atomic Scattering Factor on the Temperature Factor

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Fundamental formulae for the crystal structure factor were derived assuming aspherical atomic scattering factors. The results were applied to the refinement of several molecular complexes of the quinhydrone type. Although the  $R$  value and the atomic coordinates did not change appreciably, the anisotropic temperature factors were considerably affected. A comparison between the observed and calculated mean square displacements of the oxygen atoms indicates that the structure analysis is improved by the use of adequate aspherical atomic scattering factors.

## 1. Introduction

With recent improvements in the measurement of intensities and the development of the electronic computer, considerable attention has been paid to obtaining accurate temperature factors and electron distributions (Dawson, 1964*a*; Rae & Maslen, 1965; O'Connell, Rae & Maslen, 1966; Coppens & Coulson, 1967). For these purposes the conventional approximation to an atom of spherical symmetry is not sufficient.

The scattering factors of aspherical atoms were first introduced by McWeeny (1951), and applied to various states of bonded atoms (McWeeny, 1952; 1953; 1954; Dawson, 1961; 1964*b*). A more general formulation was derived by Freeman (1959). The effect of asphericity of the atomic scattering factors on coordinates and thermal parameters was discussed by Dawson (1964*a*) in a hypothetical model, and least-squares methods using aspherical atomic scattering factors were developed by Hirshfeld & Rabinovich (1967) and Sakurai & Ito (1968). However, the asphericity of the charge density around an atom can be represented to some extent, by a formal anisotropic thermal motion of the spherical atom. Therefore, the final residuals of the least-squares calculations with both spherical and aspherical atomic scattering factors are equally good, and it is generally quite difficult to distinguish between the effect of asphericity of the atomic scattering factor, and that of the anisotropic temperature factor.

If, however, the crystal consists of rigid molecules, individual atomic temperature factors should be expressed by the rigid body vibration of the molecule as a whole (Cruickshank, 1956; Burns, Ferrier & McMullan, 1967). In this case, the validity of the result can be judged by the internal consistency of the temperature factors of separate atoms. During the course of the investigations in our laboratory, of the quinhydrone type molecular complexes (Sakurai, 1965; Ito, Minobe & Sakurai, 1966; Sakurai, 1968) systematic inconsistencies were found in the temperature factors at the final stage of the ordinary structure analysis. In this paper, it is shown that the temperature factors are improved by the use of the aspherical atomic scattering factor.

## 2. Fundamental relations

The scattering factor of a single  $p$  orbital electron is expressed by (McWeeny, 1951)

$$f(p) = f(p)_{\parallel} \cos^2 \mu + f(p)_{\perp} \sin^2 \mu, \quad (1)$$

where  $\mu$  is the angle between the axis of the  $p$  orbital and the scattering vector  $k$ , and  $f_{\parallel}(p)$  and  $f_{\perp}(p)$  are scattering factors for the orbits parallel and perpendicular to  $k$ , respectively. The scattering factor of an atom with an incomplete  $p$  shell is also given by:

$$f = f_{\parallel} \cos^2 \mu + f_{\perp} \sin^2 \mu, \quad (2)$$

where  $f_{\parallel}$  and  $f_{\perp}$  are appropriate sums of the orbital scattering factors. If a unit vector  $u$  along the unique  $p$  orbital is defined by

$$u = ua + vb + wc,$$

then

$$\cos \mu = \frac{k \cdot u}{k} = \frac{\underline{h}u}{2 \sin \theta / \lambda}, \quad (3)$$

where the scattering vector  $k = ha^* + kb^* + lc^*$ ,  $\underline{h}$  is the row matrix  $(h, k, l)$  and  $u$  is the column matrix  $\begin{pmatrix} u \\ v \\ w \end{pmatrix}$ .

Since the direction of  $u$  changes by the symmetry operation,  $f$  changes too. Now, if a symmetry operation  $S$  is defined by the relation

$$x_s = Sx = Rx + t \quad (4)$$

where  $R$  is the rotational and  $t$  is the translational part of the symmetry operation, and  $x$  is the column matrix which expresses the coordinates, then  $u$  varies with  $R$  as

$$u_s = Ru. \quad (5)$$

Then, the crystal structure factor is

$$\begin{aligned} F &= \sum_j \sum_s f_{js} \exp(-\underline{h}B_{js}h) \exp(2\pi i \underline{h}x_{js}) \\ &= \sum_j \sum_s \left[ f_{j\parallel} \left( \frac{\underline{h}R_s u_j}{2 \sin \theta / \lambda} \right)^2 + f_{j\perp} \left\{ 1 - \left( \frac{\underline{h}R_s u_j}{2 \sin \theta / \lambda} \right)^2 \right\} \right] \\ &\quad \times \exp(2\pi i \underline{h}R_s x_j) \exp(2\pi i \underline{h}t_s) \exp(-\underline{h}R_s B_j \tilde{R}_s h), \quad (6) \end{aligned}$$

where the matrix  $B_{js}$  is introduced to express the anisotropic temperature factor,  $\tilde{R}_s$  is the transposed matrix of  $R_s$  and the summations  $\sum_j \sum_s$  are for all atoms in the asymmetric unit and all symmetry operations respectively. For the purpose of the calculations, it is a well known technique (Busing, Martin & Levy, 1962) to define a transformed index

$$\underline{h}_s = \underline{h}R, \quad (7)$$

and to express the structure factor in the form

$$F = \sum_j \sum_s \left[ f_{j\parallel} \left( \frac{\underline{h}_s u_j}{2 \sin \theta / \lambda} \right)^2 + f_{j\perp} \left\{ 1 - \left( \frac{\underline{h}_s u_j}{2 \sin \theta / \lambda} \right)^2 \right\} \right] \times \exp(2\pi i \underline{h}_s x_{js}) \exp(-\underline{h}_s B_j h_s) \exp(2\pi i \underline{h} t_s). \quad (8)$$

If the charge distribution around an atom is non-centrosymmetric the scattering factor is given by an expression (Dawson, 1964b):

$$f = f_{\parallel} \cos^2 \mu + f_{\perp} \sin^2 \mu + i f_a \cos \mu. \quad (9)$$

In this case, the crystal structure factor is

$$F = \sum_j \sum_s \left[ f_{j\parallel} \left( \frac{\underline{h}_s u_j}{2 \sin \theta / \lambda} \right)^2 + f_{j\perp} \left\{ 1 - \left( \frac{\underline{h}_s u_j}{2 \sin \theta / \lambda} \right)^2 \right\} + i f_a \frac{\underline{h}_s u_j}{2 \sin \theta / \lambda} \right] \exp(2\pi i \underline{h}_s x_{js}) \times \exp(-\underline{h}_s B_j h_s) \exp(2\pi i \underline{h} t_s). \quad (10)$$

Since the structure factors in these expressions are explicitly written in terms of independent variables, these expressions can be used as the basis for the least-squares refinement. In principle, two components of  $u$  can be changed as the parameters of the least-squares. However, in the present paper, they are fixed to the values deduced from the geometry of the molecule, because large correlations were expected between thermal parameters and components of  $u$ .

### 3. Application

Crystal structure analyses of a series of quinhydrone type molecular complexes (complexes of *p*-benzoquin-

Table 1. Observed and calculated mean square amplitudes of the atoms based on spherical atomic scattering factors ( $10^{-3} \text{ \AA}^2$  units)

The atoms are numbered according to the scheme shown in Fig. 1.

	obs	$U_{11}$ calc	difference	obs	$U_{22}$ calc	difference	$U_{33}$ obs
Hydroquinone in QH- $\beta$							
O	6	13	-7	38	40	-2	61
C(1)	11	13	-2	35	32	3	30
C(2)	19	15	4	31	30	1	36
C(3)	18	15	3	28	30	-2	34
Quinone in QH- $\beta$							
O	8	14	-6	41	42	-1	55
C(1)	18	14	4	35	33	2	31
C(2)	19	17	2	31	30	1	38
C(3)	16	17	-1	30	31	-1	36
Hydroquinone in QH- $\alpha$							
O	13	17	-4	31	33	-2	47
C(1)	14	17	-3	24	22	2	23
C(2)	24	20	4	19	19	0	28
C(3)	24	20	4	18	19	-1	31
Quinone in QH- $\alpha$							
O	13	18	-5	32	33	-1	46
C(1)	18	18	0	23	22	1	23
C(2)	22	21	1	19	19	0	30
C(3)	24	21	3	19	19	0	32
Quinone in PQ							
O	14	19	-5	44	46	-2	47
C(1)	19	19	0	34	32	2	28
C(2)	27	24	3	26	28	-2	39
C(3)	26	24	2	28	28	0	32
Quinone in QR							
O	12	15	-3	38	38	0	44
C(1)	15	15	0	24	23	1	24
C(2)	21	20	1	17	18	-1	32
C(3)	23	20	3	18	18	0	30

one) and hydroxybenzene) have been carried out in our laboratory: triclinic quinhidrone (QH- $\beta$ ) (Sakurai, 1965); monoclinic quinhidrone (QH- $\alpha$ ); pehnoquinone (PQ) (Sakurai, 1968); quinone-resorcinol (QR) (Ito, Minobe & Sakurai, 1966). Diffraction intensities, obtained by an integrating Weissenberg camera and measured by a microphotometer, were used to determine the structure. Refinements of the structures were performed by a full-matrix least-squares method using ordinary spherical atomic scattering factors. The final  $R$  values are around 10%, and these results were quite satisfactory from the usual point of view.

If the rigid body vibration of the molecule is assumed, tensors of molecular vibration can be calculated by the relation (Cruickshank, 1956)

$$|U| = |T| + (l \times r)\Omega(l \times r), \quad (11)$$

where  $U$  is the tensor expressing the mean-square amplitudes of individual atoms, and  $T$  and  $\Omega$  are the tensors expressing the translational and librational part of the molecular motion. The most probable values of  $T$  and  $\Omega$  were obtained from the observed  $U$ 's through a least-squares analysis, and the validity

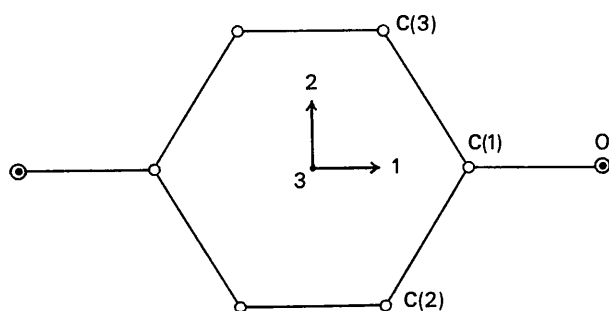


Fig. 1. Axes of the rigid body vibration.

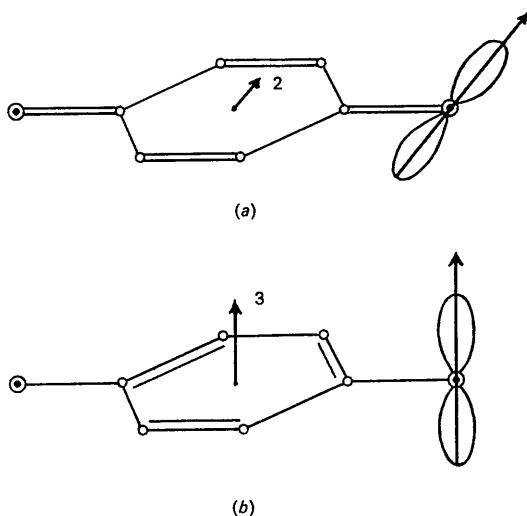


Fig. 2. Assumed lone pair directions. (a) quinone molecule; (b) hydroquinone molecule.

of the assumption of the rigid body vibration can be judged from the comparison of the observed  $U$  with those calculated from  $T$  and  $\Omega$ .

Values of  $U$  for various complexes are summarized in Table 1. Only the centrosymmetric molecules are considered in this Table, because the center of vibration for the non-centrosymmetric molecule is not uniquely determined. The axes of the molecular vibration are shown in Fig. 1. Since the shapes of the molecules are quite simple, the  $U_{33}$  components can be exactly fitted by  $T$  and  $\Omega$ ; therefore, only the observed values are listed in the Table. Compared with the diagonal components, the off-diagonal ones were found to be generally small, being of the order of the estimated standard deviations, and they were omitted from the Table.

Agreement between the observed and calculated  $U$  are generally good. However,  $U_{11}$  components of the oxygen atoms, that is, the mean square displacements of the atoms along the C-O direction are systematically smaller than the calculated values. If the stretching vibration along the C-O direction is appreciable, the mean square displacement due to the internal vibration should be additive with that of the rigid body vibration. Since the observed displacement is smaller than the calculated one, the difference cannot be attributed to the internal vibration. Although there are several possibilities of experimental error, such as absorption or spectral splitting, which may affect the absolute values of the temperature factors, none of these is enough to explain the systematic discrepancies found only in the oxygen atoms in a particular direction. The most probable reason was considered to be an inadequate form of the atomic scattering factor. Therefore, these structures were refined by least-squares method based on equation (8).

It was stated by McWeeny (1951) and Dawson (1964b), that for the quadrivalent carbon, the total scattering factor is independent of the state of hybridization, and is spherically symmetric, unless the higher order effect of interatomic bonding is considered. Then, only the asphericity of the oxygen atom was considered. In a simplified model, the oxygen atom has four electrons in the three  $2p$  orbitals; two  $p$  orbitals with one electron in each are used to form chemical bonds, and the third orbital with the other two electrons forms a lone pair orbital. Therefore, the atomic form factor is

$$\begin{aligned} f_{||} &= f(s) + 2f_{||}(p) + 2f_{\perp}(p) \\ f_{\perp} &= f(s) + f_{||}(p) + 3f_{\perp}(p), \end{aligned} \quad (12)$$

where the unique axis is along the lone pair orbital. For present calculations, the direction of the lone pair was assumed to be along axis 2 for the carbonyl oxygens, and along axis 3 for the hydroxyl oxygens respectively (Fig. 2). Numerical values of  $f_{||}$  and  $f_{\perp}$  used for these calculations are those given by Freeman (1959). A few strong low order reflexions, which are appreciably affected by extinction, were eliminated.

## 4. Results and discussion

(a) *R and R1 indices*

The least-squares refinement was performed to minimize the factor

$$R1 = \sum w(|F_o| - |F_c|)^2 \quad (13)$$

where  $w$  is the weight of the observation. Here, unit weights were given to all the observations used. The final  $R$  and  $R1$  indices for both spherical and aspherical cases are compared in Table 2. It is well known that at the final stage of refinement, small variation of the  $R$  value have no significance.  $R1$  values show a slight reduction in this case.

Table 2. Comparison of the  $R$  and  $R1$  factors after the final cycle of the full-matrix least squares

Crystal	$R$ (%)		$R1$ (relative values)	
	Spherical	aspherical	spherical	aspherical
QH- $\beta$	9.8	9.4	1.00	0.93
QH- $\alpha$	9.3	9.5	1.00	0.94
PQ	10.3	10.5	1.00	0.88
QR	10.9	10.9	1.00	1.00

(b) *Changes in coordinates and bond distances*

A few examples of the change in coordinates are shown in Table 3. These variations are smaller than the standard deviations, and have no systematic tendency. Therefore, the change in coordinates and corresponding bond distances is not significant.

Table 3. Effect of asphericity on the atomic coordinates of the quinone in QR ( $\times 10^4$ )

The values are corrected for the effect of the rigid body librations.

		Spherical	Aspherical	Change	e.s.d.
O	$x/a$	0705	0705	0	3
	$y/b$	-3501	-3500	1	7
	$z/c$	1111	1111	0	4
C(1)	$x/a$	0391	0391	0	4
	$y/b$	-1875	-1876	-1	10
	$z/c$	0585	0586	1	5
C(2)	$x/a$	-0088	-0088	0	4
	$y/b$	-0087	-0087	0	12
	$z/c$	1242	1241	-1	5
C(3)	$x/a$	-0467	-0467	0	4
	$y/b$	1675	1673	-2	10
	$z/c$	0680	0680	0	5

(c) *Change of thermal parameters*

The anisotropic temperature factor used is of the form

$$\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2klB_{23} + 2lhB_{13} + 2hkB_{12})]$$

The changes of some  $B$  values of the oxygen atoms exceeded three times their standard deviations, and

those of the carbon atoms were found to be insignificant. Typical examples are shown in Table 4. Some of the ellipsoids of thermal vibration for both cases are compared in Fig. 3. As is clearly seen on these Figures, the displacements of the oxygen atoms have remarkably decreased in the lone pair direction (along axis 2 in the quinone, axis 3 in the hydroquinone), and increased in the other directions. The tensors of the rigid body vibration calculated from these temperature factors are shown in Table 5, together with the results for the spherical case. The small off-diagonal components are omitted from the Table. Among the diagonal components,  $\Omega_{33}$  of the quinones changed significantly.

Table 4. Effect of asphericity on the thermal parameters of the quinone in QH- $\alpha$  ( $\times 10^4$ )

		Spherical	Aspherical	Change	e.s.d.
O	$B_{11}$	148	158	10	8
	$B_{22}$	123	133	10	11
	$B_{33}$	48	36	-12	4
	$B_{12}$	-68	-62	6	8
	$B_{13}$	22	15	-7	4
	$B_{23}$	-20	-9	11	5
C(1)	$B_{11}$	84	81	-3	8
	$B_{22}$	112	109	-3	14
	$B_{33}$	36	34	-2	4
	$B_{12}$	-12	-12	0	10
	$B_{13}$	18	17	-1	5
	$B_{23}$	-7	-6	1	7
C(2)	$B_{11}$	97	94	-3	9
	$B_{22}$	141	136	-5	15
	$B_{33}$	30	29	-1	4
	$B_{12}$	-15	-16	-1	10
	$B_{13}$	13	12	-1	5
	$B_{23}$	2	3	1	7
C(3)	$B_{11}$	94	92	-2	9
	$B_{22}$	148	144	-4	17
	$B_{33}$	35	33	-2	4
	$B_{12}$	-15	-17	-2	11
	$B_{13}$	14	13	-1	5
	$B_{23}$	14	14	0	7

The observed and calculated mean square amplitudes of the atoms are summarized in Table 6. Compared with the value in Table 1, the agreement between  $U_{\text{obs}}$  and  $U_{\text{calc}}$  has generally been improved and, especially, the systematic discrepancies of  $U_{11}$  of the oxygen atoms have been reduced to the order of the average deviations.

(d) *Difference-Fourier synthesis*

Although the effect of asphericity on the temperature factor was significantly large, the effect on the crystal structure factor,  $F_c$ , was very small, the difference being less than one per cent. In fact, only a few very weak reflexions among a set of about one thousand had different signs, and almost identical electron density maps were obtained for both cases. Also, the general features of the difference electron density maps were the same for both cases. An example is shown in Fig. 4, where the residual peaks around the oxygen atom are slightly

Table 5. *Translational and librational tensors of the rigid body vibration* [ $T$  in  $10^{-3} \text{ \AA}^2$  and  $\Omega$  in (degrees)<sup>2</sup>]

The figures in parentheses are the standard deviations.

	$T_{11}$	$T_{22}$	$T_{33}$	$\Omega_{11}$	$\Omega_{22}$	$\Omega_{33}$
Hydroquinone in QH- $\beta$						
spherical	13 (2)	29 (2)	20 (4)	28 (11)	18 (3)	4.7 (1.7)
aspherical	13 (1)	28 (1)	20 (3)	28 (7)	16 (2)	5.7 (1.1)
Quinone in QH- $\beta$						
spherical	14 (1)	30 (2)	21 (4)	29 (8)	16 (2)	5.6 (1.5)
aspherical	16 (1)	30 (1)	20 (3)	32 (6)	18 (2)	2.4 (1.0)
Hydroquinone in QH- $\alpha$						
spherical	17 (1)	18 (2)	15 (3)	29 (8)	14 (2)	6.4 (1.3)
aspherical	18 (1)	17 (1)	17 (2)	24 (6)	10 (1)	7.8 (0.9)
Quinone in QH- $\alpha$						
spherical	18 (1)	18 (1)	14 (3)	32 (6)	15 (2)	7.2 (1.1)
aspherical	19 (1)	18 (1)	11 (3)	36 (5)	18 (2)	3.6 (1.0)
Quinone in PQ						
spherical	19 (1)	26 (2)	20 (4)	28 (8)	12 (2)	8.9 (1.4)
aspherical	20 (1)	27 (1)	19 (3)	28 (7)	14 (2)	4.8 (1.2)
Quinone in QR						
spherical	15 (1)	16 (1)	16 (3)	27 (7)	13 (2)	10.2 (1.2)
aspherical	17 (1)	17 (1)	15 (3)	30 (6)	16 (2)	6.1 (1.1)

Table 6. *Observed and calculated mean squares amplitudes of the atoms based on aspherical atomic scattering factors* ( $10^{-3} \text{ \AA}^2$  units)

	obs	$U_{11}$ calc	difference	obs	$U_{22}$ calc	difference	$U_{33}$ obs
Hydroquinone in QH- $\beta$							
O	10	13	-3	40	42	-2	57
C(1)	11	13	-2	35	32	3	29
C(2)	18	16	2	30	29	1	36
C(3)	18	15	3	28	29	-1	34
Quinone in QH- $\beta$							
O	13	16	-3	34	35	-1	59
C(1)	17	16	1	33	31	2	31
C(2)	18	17	1	30	30	0	38
C(3)	18	17	1	29	30	-1	37
Hydroquinone in QH- $\alpha$							
O	17	18	-1	34	35	-1	39
C(1)	14	18	-4	23	22	1	22
C(2)	23	21	2	19	18	1	27
C(3)	23	21	2	17	18	-1	31
Quinone in QH- $\alpha$							
O	17	19	-2	24	26	-2	50
C(1)	18	19	-1	22	20	2	23
C(2)	21	20	1	18	18	0	30
C(3)	23	20	3	18	18	0	32
Quinone in PQ							
O	17	20	-3	36	37	-1	49
C(1)	18	20	-2	32	30	2	28
C(2)	26	23	3	26	28	-2	38
C(3)	24	23	1	29	28	1	31
Quinone in QR							
O	15	17	-2	29	30	-1	48
C(1)	16	17	-1	23	21	2	24
C(2)	21	20	1	17	18	-1	32
C(3)	23	20	3	19	18	1	30

smaller for the aspherical case, but the difference is less than the depth of the negative peaks.

Thus, the difference in the atomic scattering factor of oxygen was almost completely compensated by the apparent temperature factor of the same atom. This is to be expected, because both of the ratios,  $f_{||}/f(\text{spher-}$

ical) and  $f_{\perp}/f(\text{spherical})$ , can be well fitted by a Gaussian form,  $\exp[-(\text{const.})s^2]$ , in the Cu  $K\alpha$  range of  $s$ .

(e) *Comparison with other work*

Two sets of structure data from other authors on crystals of component molecules were examined with

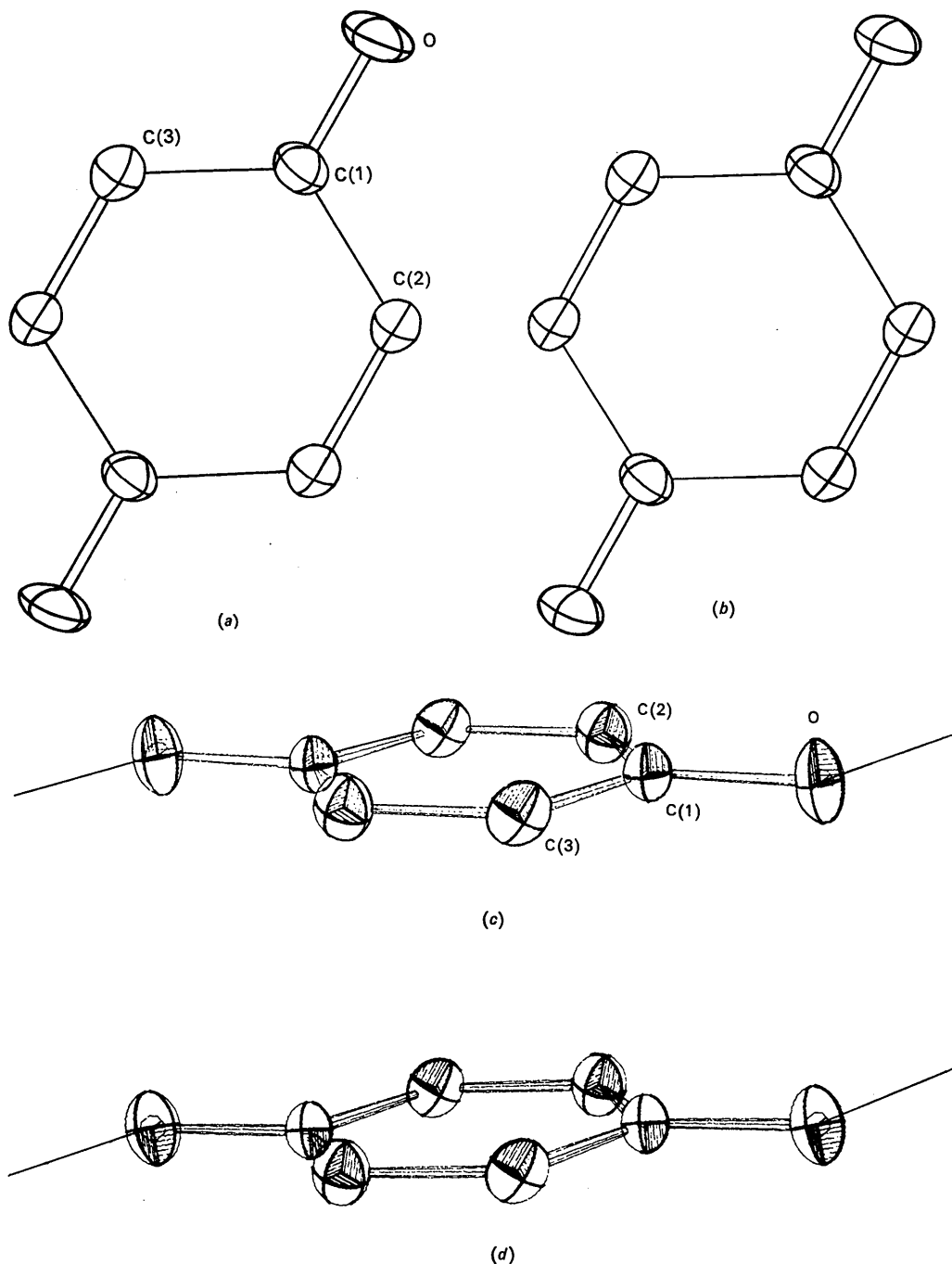


Fig. 3. Thermal ellipsoids of the spherical and the aspherical atoms. (a) and (b); the quinone in QR projected on the molecular plane: (a) spherical, (b) aspherical. (c) and (d); the hydroquinone in QH- $\alpha$  projected along the  $c$  axis: (c) spherical; (d) aspherical.

respect to the asphericity of the oxygen atoms: quinone (Trotter, 1960) and  $\gamma$ -hydroquinone (Maartmann-Moe, 1966).

For the present purpose, the structure of quinone was again refined by a full-matrix least-squares procedure based on the  $F_o$  values listed in the reference. Spherical atomic scattering factors were used, and the final  $R$  value was reduced to 11.2% from the original 12.4%. Maartmann-Moe analysed and refined the crystal structure of  $\gamma$ -hydroquinone by a full-matrix least squares with the final  $R$  value of 8.5%. The asymmetric unit of the cell contains two independent hydroquinone molecules.

The thermal parameters of the three molecules were analyzed by the same procedure as described in § 3. The results are given in Table 7. As is evident from the Table, the observed values of  $U_{11}$  of the oxygen atoms in these molecules are systematically smaller than the calculated ones, in agreement with our results in Table 1.

In structural studies of cytosine (Barker & Marsh, 1964) and anthraquinone (Lonsdale, Walley & El Sayed, 1966), the existence of the large out-of-plane, non-rigid body vibrations of the ketonic oxygen was reported. This effect could not be examined in the present study because, as stated in § 3, the shape of

Table 7. Observed and calculated mean square amplitudes of the spherical atoms from other work ( $10^{-3} \text{ \AA}^2$  units)

The atoms are numbered according to the scheme shown in Fig. 1.

	obs	$U_{11}$ calc	difference	obs	$U_{22}$ calc	difference	$U_{33}$ obs
Quinone in quinone (Trotter)							
O	42	51	-9	97	95	2	158
C(1)	57	51	6	49	61	-12	79
C(2)	69	62	7	51	50	1	86
C(3)	59	62	-3	59	50	9	93
Hydroquinone(1)* in $\gamma$ -hydroquinone (Maartmann-Moe)							
O	19	23	-4	41	40	1	63
C(1)	23	23	0	24	28	-4	26
C(2)	29	26	3	23	25	-2	24
C(3)	27	26	1	31	25	6	35
Hydroquinone(2) in $\gamma$ -hydroquinone (Maartmann-Moe)							
O	16	20	-4	56	56	0	57
C(1)	24	20	4	24	28	-4	28
C(2)	30	27	3	23	21	2	32
C(3)	26	27	-1	22	21	1	36

\* The most probable values of the librational tensor of this molecule turned out not to be positive definite.

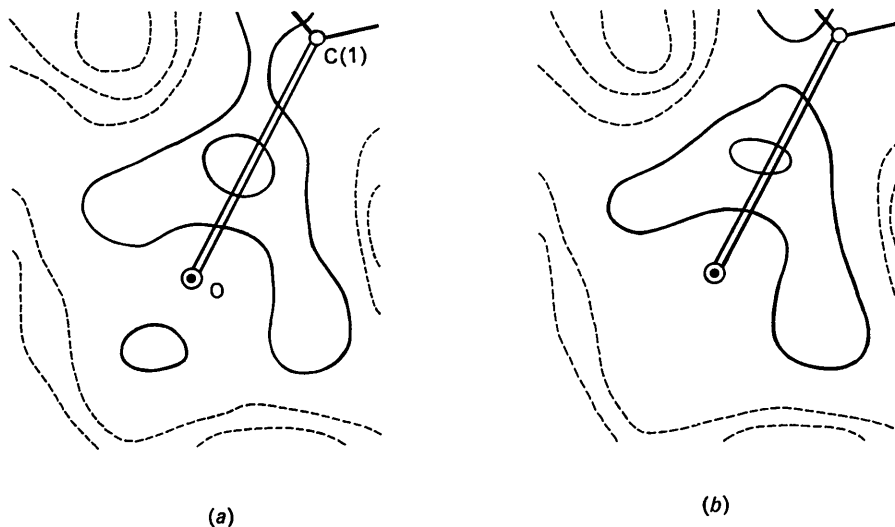


Fig. 4. Part of the difference electron density section through the molecular plane of the quinone in QR. Contour interval is  $0.1 \text{ e. \AA}^{-3}$ ; full lines are positive; dashed lines are negative; zero lines are omitted. (a) spherical; (b) aspherical.

the present molecule is too simple to distinguish the out-of-plane oxygen vibration from the rigid body libration of the whole molecule.

### 5. Concluding remarks

In the present calculations, ordinary spherical scattering factors were used for the carbon and hydrogen atoms, and the effect of bond scattering factor (McWeeny, 1952) and the possibility of the charge transfer as a result of the hydrogen bond (Tsubomura, 1954) were completely neglected. In this respect, the present treatment is still too naive to discuss the distribution of valence electrons. Also, an  $R$  value of around 10% is sufficient to determine the atomic positions, but not enough to discuss the effect of bonding. This will be the limit of the ordinary photographic measurement of diffraction intensity.

One aim of this paper, however, is to show that even at this level of accuracy the introduction of the aspherical atomic scattering factor can improve the results of structure analyses.

In the present study, the changes in bond distances and angles were negligible. However, this result should not be considered to be general. If an atom is not centrosymmetric, the imaginary component in equation (10) will introduce the shift of the positional parameter, as discussed by Dawson (1964a).

It can be seen from Table 6, that there still remains a small but systematic discrepancy of the  $U_{11}$  component of the oxygen atom. This may be due to the effect of bonding.

In order to clarify these points, accurate counter measurements at various temperatures are now being planned.

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## The Crystal Structure of Thymine

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The crystals of thymine anhydrate are monoclinic with the space group  $P2_1/c$ . The unit-cell dimensions have been reported as follows:  $a=12.87$ ,  $b=6.83$ ,  $c=6.70$  Å,  $\beta=105^\circ$  and  $Z=4$ . The structure was determined and refined by the three-dimensional least-squares method. The final  $R$  index for 724 observed reflections is 0.149 and the standard deviations in the positional parameters are about 0.011 Å. Pairs of molecules related by the twofold screw axis are connected by the two N-H...O=C hydrogen bonds and they form infinite chains along the  $b$  axis.

### Introduction

Thymine is an essential component of deoxyribonucleic acid (DNA) molecule, and its structure is of par-

ticular importance in understanding the mechanism of the biological functions of DNA. The crystal of thymine monohydrate has been analysed by Gerdil (1961), but only the crystal data of thymine anhydrate are re-